

GPO PRICE \$ _____

CFSTI PRICE(S) \$ _____

Hard copy (HC) \$ 1.00

Microfiche (MF) .50

77 653 July 65

(NASA TT F-8494)

STUDY OF CYANIC ACID SYNTHESIS BY FIXED CATALYST METHOD

by

M. Otake, M. Nakagawa, et al.

Translated from Kogyo Kagaku Zasshi, Vol. 59, No. 1, 121-124, 1956

N66 27225

(ACCESSION NUMBER)

(PAGES)

(THRU)

(CODE)

(CATEGORY)

(NASA CR OR TMX OR AD NUMBER)

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

WASHINGTON D.C.

July 1963

STUDY OF CYANIC ACID SYNTHESIS BY FIXED CATALYST METHOD

(Received 6 September 1955)

Kogyo Kagaku Zasshi
(Journal of Industrial Chemistry)
59, No. 1, 121-124 (1956)

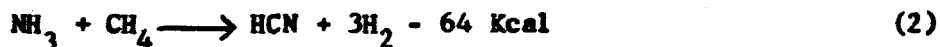
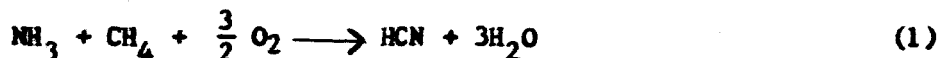
M. Otake*
M. Nakagawa*
T. Ohara**
H. Harada*
M. Ninomiya*

* Osaka City College, Department of Science and Engineering

** Japan Catalytic Chemical Industrial Co., Ltd., Fukita City, Otabimachi

I. Introduction

The attempt to synthesize cyanic acid from ammonia and methane or other gaseous hydrocarbons is not new, and there are numerous reports and patents on the subject. The first well known method consists of synthesis from methane, ammonia, and air or oxygen passed over a hot screen made of a platinum group metal, according to the reaction indicated in Eq. (1). This technique stems from Andrussov's basic research⁽¹⁾, and the reaction is exothermic and similar to that for nitric acid synthesis where ammonia is oxidized.



The second method of cyanic acid synthesis consists of passing a mixture of hydrocarbons and ammonia over a catalyst heated to a high temperature.⁽²⁾ This reaction proceeds as shown in Eq. (2), the reaction is endothermic, the products are cyanic acid and hydrogen, and it has the advantage of not only producing relatively concentrated cyanic acid in a single operation but of allowing easy separation of cyanic acid as a result of the absence of a water-soluble acidic gas such as carbon dioxide gas. The exhaust gas is rich in hydrogen, and it can be used either as a source of hydrogen or simply for fuel. Our group undertook research on the second method with the aim of increasing catalytic efficiency, cyanic acid yield, and of lowering the reaction temperature. The present paper reports only on the basic studies performed with a fixed catalyst.

II. Method of Experiment

The methane used in our experiment came from natural gas from Mohara-machi in Chiba Prefecture, while the ammonia used was the usual commercial grade available in cylinders. The composition of the natural gas was as follows:

Table 1

Sample	CH ₄	CO ₂	H ₂	N ₂
1	90.9	0.6	6.8	1.7
2	91.3	0.6	6.2	1.9
3	90.3	1.6	6.5	1.6
4	90.9	1.3	5.2	2.6

In the experiment, the flow method was used so that the cyanic acid yield and the decomposition of the ammonia could be measured as a function of time, in other words, the efficiency of the catalyst could be investigated.

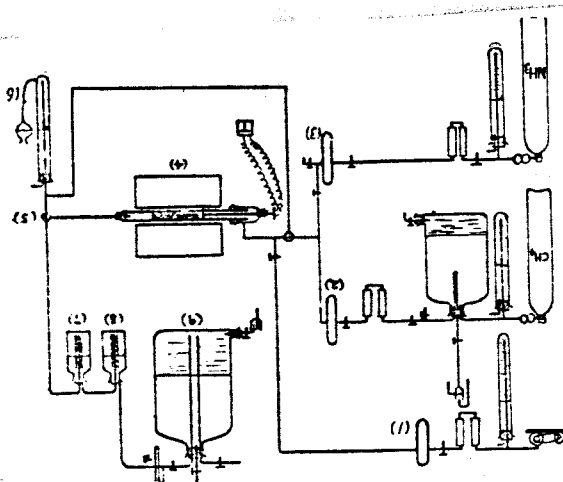


Figure 1.

The experimental apparatus is sketched in Figure 1. Flow meters (2) and (3) are used to accurately measure the amount of methane and ammonia gases which are introduced into a fused quartz reaction tube heated by the oven (4) with silicon carbide heater elements. The exhaust gas escapes through the three-way cock (5) and the regulator (6). After a stationary state has been reached, the cock is switched over and the gas is allowed to pass for 60 minutes through a 20% NaOH solution (7) and 5% H₂SO₄ solution (8) in order to absorb all of the cyanic acid

formed as well as the remnant ammonia gas. The residual gas is collected (9), its volume measured, and if necessary, it is analyzed. Following this first 60-minute period of gas collection, the cock (5) is turned and the gas is exhausted for 60 minutes with the reaction being permitted to continue without any change, after which the reaction product gas is again collected for another 60 minutes. In other words, the reaction product gas was collected every other hour. Parts of solutions (7) and (8), which contain fixed cyanic acid and ammonia respectively, were analyzed, the former by the Volhard and the latter by the Kjeldahl method, and the cyanic acid yield and the degree of ammonia decomposition were determined according to the following formulae:

$$\text{Cyanic acid yield} = \frac{\text{cyanic acid produced (mol)}}{\text{ammonia consumed (mol)}} \times 100$$

$$\text{Ammonia decomposition rate} = 100 - \frac{[\text{HCN yield} + \text{ammonia recovered (mol)}]}{\text{ammonia consumed (mol)}} \times 100$$

Any carbon coming from the decomposition of the methane and deposited on the catalyst was burnt out by introducing air through the air flowmeter (1). This process will be referred to simply as "air burning" during the remainder of this paper.

III. Experimental Results

The catalyst used was either in the form of pellets, or small particles crushed to about 3 mm size. About 35 cc of this was packed into a 23 mm I.D. fused quartz reaction tube. The temperature near the center of the reaction layer was maintained at 1050°C, with the rates of flow of methane and ammonia being fixed at 200 cc/min and 100 cc/min respectively.

1. Alumina as Catalyst

The alumina used was prepared according to Makishima's method⁽³⁾ and it was treated at 600°C in a flow of ammonia gas for 3 minutes. The results of cyanic acid synthesis using this catalyst are as shown in Figure 1. It can be seen that the cyanic acid yield decreases with time after reaching an early peak, and there is no recovery even following the air burning at 18 hours. The rate of ammonia decomposition is seen to increase rapidly with decreasing cyanic acid yield. Reduced catalyst activity is probably due either to sintering of the alumina, or to transition of the alumina to a more stable form. This loss of catalyst activity is even more pronounced, as can be seen in Figure 3, for alumina prepared by precipitation from a pure sodium aluminate solution at pH 7 (HCl), this precipitate being filtered and rinsed on a suction funnel. It is assumed that this drastic change in activity is due to inadequate washing of the precipitate and the presence of impurities.

The results of this experiment have at least indicated that the decrease in catalyst activity might be avoided by the addition of a second element to the catalyst, and with this purpose in mind, the following experiment was performed with an alumina-silica two-component catalyst.

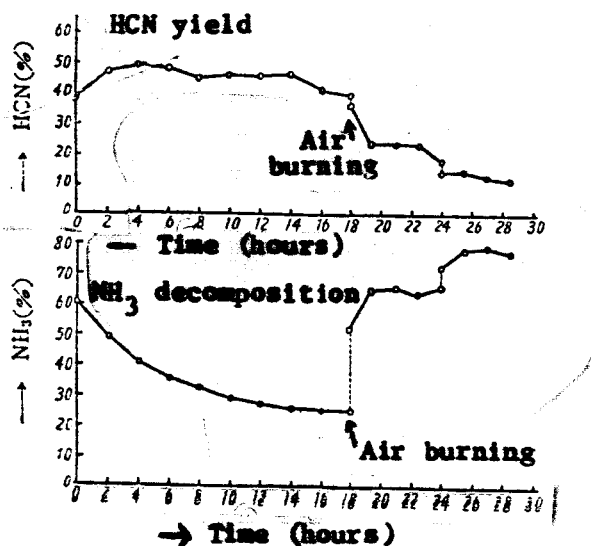


Figure 2.

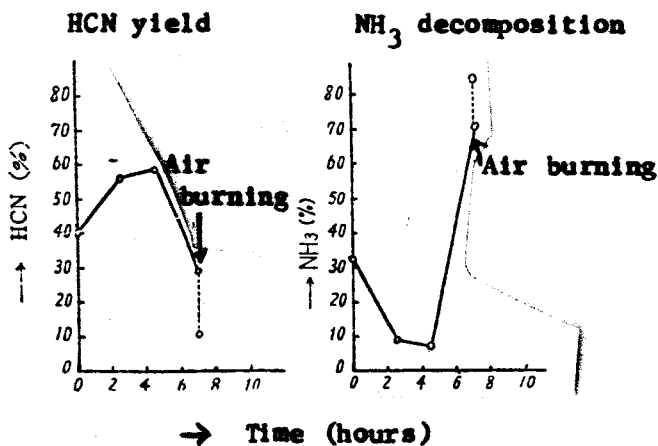
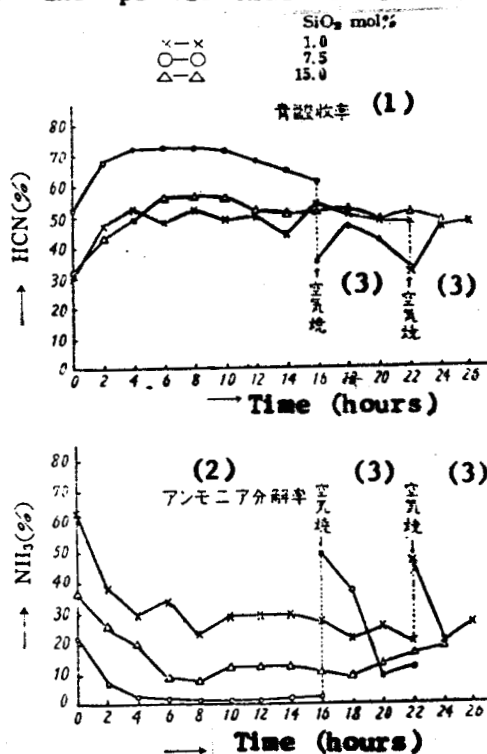


Figure 3.

2. Alumina-Silica Catalyst

This catalyst was prepared by adding HCl to an aluminum chloride solution, further adding a measured amount of sodium silicate, then precipitating aluminum hydroxide and silicic acid by titrating ammonia water while stirring the solution. The precipitate was well washed with water, dried, and pulverized. Different proportions of silica to alumina, namely 1, 5, 6, 7, 7.5, 10, 15, and 20 mol% were tried, a typical result being shown in Figure.4. Aside from the actual differences in activity between the different mixtures, the general trend for this catalyst is for the activity to have a maximum at between 4 and 8 hours, after which the activity declines gradually. If we take cyanic acid yield averaged for the interval 4-to-10 hours and compare the yield values for different mixtures, one obtains the result shown in Figure 5, where the activity is maximum for a silica content of 7 to 7.5 mol%. This proves that silica does indeed improve catalyst activity.



Legend:
 (1) HCN yield
 (2) NH₃ decomposition
 (3) Air burning

Figure 4.

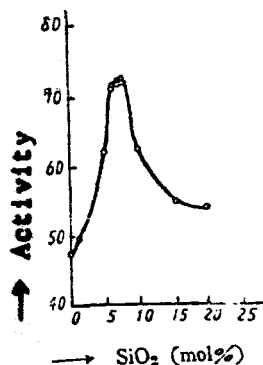


Figure 5.

The characteristic time variation in the activity of this alumina-silica catalyst, whereupon the activity gradually increases to a maximum then slowly decreases, can possibly be explained by the occurrence of a solid phase reaction between alumina and silica at high temperatures. In other words, activity is maximum during some intermediate unstable state, and the decline in activity is probably due to the gradual formation of stable aluminum silicate. The following experiment proves this assumption.

In the experiment, a mixture containing 7.5 mol% silica was heated at 1050°C in a muffle oven, the batch was removed at certain intervals, cooled, and pulverized. 2.00 gram of this was added to 50 cc of 0.04% eosin solution, shaken, allowed to sit for 24 hours, and then the clear solution was drawn off after centrifuging, and the amount of eosin adsorbed by the catalyst was measured by means of colorimetry. The relation between the length of time heated and the amount of eosin adsorbed is shown in Figure 6, where it can be seen that there is maximum adsorption for 3 to 6 hours of heating. The curve is quite similar to that indicating catalyst activity, and it proves that with the progression of a solid phase reaction between the alumina and the silica, a meta-stable intermediate state exists at which both adsorption and catalyst activity are maximum, but following which period, the system tends towards stability and a decline in adsorption and catalytic activity.

Despite the fact that alumina-silica can be quite efficient as a catalyst for cyanic acid synthesis, its practical value was found to be limited due to its lack of durability.

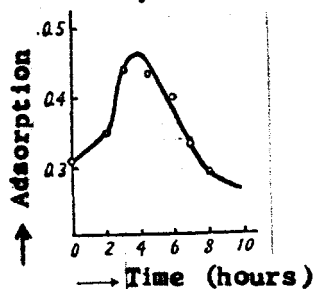


Figure 6

3. Alumina-Thoria Catalyst

As related in the previous section, silica was found to have a solid phase reaction with alumina which was detrimental to its use as a catalyst, and we therefore turned next to thoria which was expected to less likely react with alumina.

This catalyst was prepared by adding a measured quantity of sodium nitrate to aluminum chloride solution, then precipitating the hydroxides of aluminum and thorium simultaneously by the addition of ammonia solution while stirring, and then the precipitate being thoroughly rinsed. It was later discovered that even a better precipitate could be obtained by adding thorium chloride or nitrate in HCl solution to sodium aluminate solution. (Note: The experimental results using the last method are given in a later paper.)

Six different mixtures of alumina and thoria were prepared, the thoria content varying as 1, 2, 2.6, 3, 3.5, and 5 mol%. It was discovered that thoria concentration had little effect on catalyst activity, and that, as shown in Figure 7, the cyanic acid yield decreased gradually with time but recovered with air burning. This apparently indicates that the decline in activity is due to soot, from methane decomposition, being adsorbed by the catalyst. The residual gas, that is, the gas remaining after removal of ammonia and cyanic acid, amounted to about 28 liters/hour, and an analysis of this residual gas, as shown in Table 2, indicates considerable thermal decomposition of methane.

Table 2.

	N ₂	H ₂	CH ₄
Early period	4.2	92.0	3.8
Later period	2.7	85.5	11.8

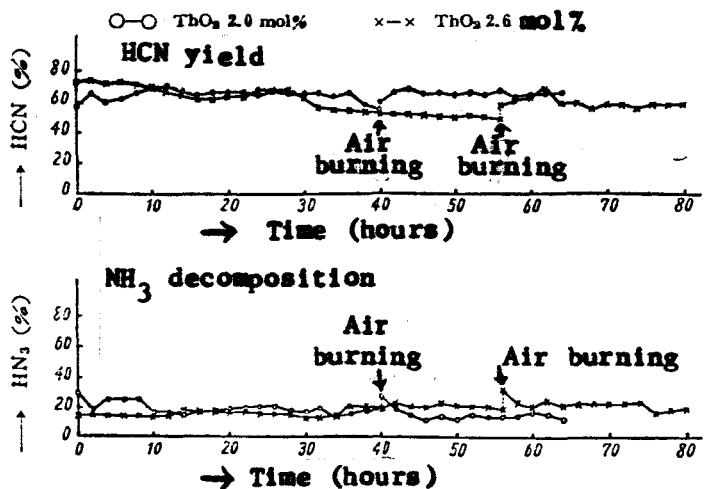


Figure 7.

The above experiments indicate that alumina-thoria prepared in the manner described has roughly the catalyst characteristics suitable for cyanic acid synthesis from methane and ammonia.

4. Effect of Sulfur Compounds (Note: Japanese Patent pending, Declaration 1955-3360.)

Since sulfur compounds could be present in hydrocarbons used as raw materials, such as in the case of petroleum cracking gas, the effect of sulfur on cyanic acid yield was investigated by the deliberate introduction of small amounts of HS or carbon disulfide into the original methane. Surprisingly, the yield of cyanic acid was found to be greatly increased by the presence of sulfur. Since the use of either hydrogen sulfide or carbon disulfide gave the same result, we used the latter primarily in the current experiment. The apparatus shown in Figure 1 was modified so that methane and ammonia could be independently introduced into the reaction tube, and the device shown in Figure 8 was employed for the addition of carbon disulfide. In the latter figure, (1) is the atomizer for the carbon disulfide, and the amount of vapor of carbon disulfide is controlled by means of adjusting cock (2) and thus regulating the flow of methane through the carbon disulfide.

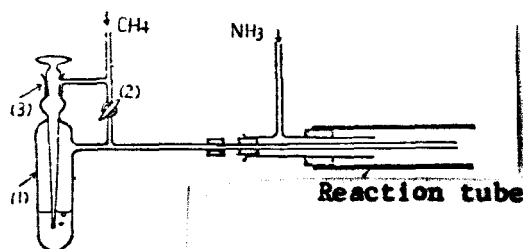


Figure 8.

In Figure 9 is shown an example of cyanic acid yield averaging about 60% with an alumina-thoria catalyst (thoria content 1 mol%), and how this yield increases to 80% with the addition of carbon disulfide but also decreases immediately to the original 60% level when it is discontinued. The sulfides added to the methane turn up in the reaction product gas as hydrogen sulfide, and this is analyzed in the following manner: The solution to be analyzed, which contains sodium cyanide and sodium sulfide, is made alkaline with an excess of ammonia water, to which is then added a measured excessive amount of 1/10 N- AgNO_3 solution. The precipitate is filtered and well rinsed. The filtrate and rinse water are combined and made acidic with 6N- HNO_3 , which then precipitates AgCN . This is filtered and rinsed, and the excess Ag ion in the new filtrate and rinse water is then measured by the Volhard method. The silver sulfide is dissolved in 6N- HNO_3 , thinned with water, and measured by the Volhard titration method. If the AgNO_3 added is V cc, the titrated

value of silver sulfide is v_s cc, and the titrated amount of AgCN is v_{CN} cc, then the amount of silver ion consumed by the cyanide ion is given by

$$v = V - (v_s + v_{CN})$$

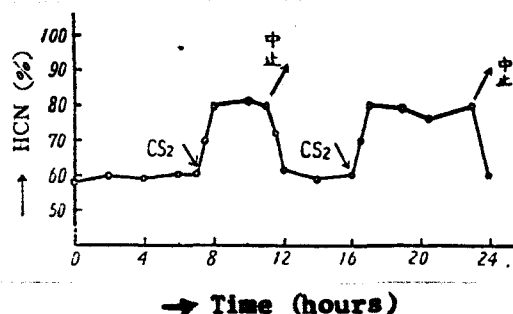


Figure 9.

IV. Conclusions

With respect to the process for cyanic acid synthesis involving the reaction of methane and ammonia in a volume ratio of 2:1 at a temperature of 1050°C, the results of research on catalysts for this reaction are summarized as follows:

(1) The ordinary alumina catalyst is unsuitable for practical use from the standpoints of cyanic acid yield and durability.

(2) In the case of an alumina-silica catalyst, the silica distinctly aided the catalytic action, but despite the high cyanic acid yield which could be obtained, catalytic activity declined with time from which recovery could not be effected. The cause of this decline in activity was attributed to a solid phase reaction between the alumina and the silica.

(3) Alumina-thoria as a catalyst produced fairly high cyanic acid yield. The decline in catalytic activity due carbon adsorption was easily remedied by air-burning of the carbon.

(4) It was discovered that a small amount of carbon disulfide or hydrogen sulfide in the raw material gases increased the cyanic acid yield considerably.

(Lecture presented at 8th annual meeting of the Japan Chemical Society, April 1955)

The authors would like to thank Prof. Tatsusaburo Hara for his kind advice, and also S. Kurosawa for his assistance during the early part of this study. This research was supported in part by an institutional research grant from the Ministry of Education in 1952, and also by funds provided by the Japan Catalytic Chemical Industrial Co., Ltd., to whom the authors are also indebted.

References:

- (1) L. Andrussov, Angew. Chem., 48, 593 (1935)
- (2) For example, E. P. 335,585; 349,958 etc.
- (3) Makishima, Journ. Chem. Japan., 62, 770 (1941).